ABSTRACT

A simple tumbling model for the dielectric relaxation of a series of oligomeric alcohols

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A simple model is developed to describe the dielectric relaxation of short chain oligomeric polar molecules based on the assumption that, as temperature increases, a transition from a hindered librational motion to a quasi-free rotational tumbling of the molecules will occur. The model addresses the question of whether the tumbling configuration is fully extended, a random coil, or an intermediate state. A comparison of the model with experimental results obtained by time domain dielectric spectroscopy (TDDS) for a homologous series of oligomeric normal alcohols ($C_nH_{2n+1}OH$) shows, somewhat surprisingly, that the extended chain configuration agrees with the data quite well. Up to the longest alcohol investigated (dodecanol, n=12) there was no evidence of a shift toward the random coil configuration.

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INTRODUCTION

As temperature T increases the dielectric relaxation of an oligomeric alcohol molecule can be usefully envisioned as having a maximum loss peak (ϵ'') when its hindered librations become end-over-end tumbling motions of a quasi-rigid entity of moment of inertia I. Although this model is stripped to its barest simplicity it can be justified in part by considering, in polar coordinates, the Schrodinger equation,

$$\frac{1}{\sin\Theta}\frac{\partial}{\partial\Theta}\left[\sin\Theta\,\frac{\partial\psi}{\partial\Theta}\right] + \frac{1}{\sin^2\Theta}\left[\frac{\partial^2\psi}{\partial\phi^2}\right] + \frac{8\pi^2 I\,(E-V)\psi}{h^2} = 0 \qquad (1a)$$

for a rigid rotator with a periodic potential for rotation

$$V = V_o\,(1 - \cos n\Theta). \qquad (1b)$$

The methods for treating this problem were developed long ago by Wilson [1] and Stern [2]. For the case of n = 2, the results may be described in terms of two limiting cases. One limiting case occurs at low temperature and the potential can be considered as a series of parabolic minima about which harmonic oscillations occur. The other limiting case corresponds to high temperature so that the wave functions ψ and energy E correspond to those of a free rotator. For n = 2, the transition between oscillation and rotation takes place when $T_o = 2V_o/k$. Two possible chain conformations are considered, namely a fully extended molecule and a molecule with a random orientation of bond vectors (random coil). Equations are developed for both cases and are compared with experimental data obtained through time domain dielectric spectroscopy (TDDS). The implications of the results are then discussed.

DEVELOPMENT OF THE TUMBLING MODEL

The simplest representation of the model corresponds to the assumption of a rotational equipartition of energy, so that $\frac{1}{2}I\omega^2 \sim kT$ or

$$\omega^2 \sim 2kT/I \tag{2}$$

where $\omega = 2\pi f_m$ corresponds to the frequency f_m of maximum dielectric loss.

Figure 1 is a schematic of an alcohol molecule for the fully extended case where the spheres of mass m are assumed to be groups of carbons, hydrogens, and oxygens and the OH end group is treated as equivalent to the other mass centers on the chain.

From Fig. 1 and the definition of I,

$$I = \Sigma m_i r_i^2 \sim \int_{-R/2}^{R/2} \rho_\ell r^2 dr \tag{3}$$

$$= \frac{1}{12} \rho_\ell R^3 = \frac{1}{12} \frac{mR^3}{a} \tag{4}$$

where the average linear density is taken to be $\rho_\ell = m/a$. For a fully extended alcohol molecule $R_e = na$, so that

$$\omega = [24akT/mR_e^3]^{1/2} = K'_e T^{1/2} n^{-3/2} \quad (5)$$

Thus, converting to the peak frequency $f_m = \omega/2\pi$ and adsorbing the various constant parameters in a single constant K_e, Eq. 5 can be expressed as

$$\log n = -(2/3) \log f_m + (2/3)[\log K_e + \tfrac{1}{2} \log T] \quad (6)$$

For a fully extended alcohol molecule the model yields a linear equation with slope of -2/3 when log n vs log f_m is plotted for a given temperature.

On the other hand, for a random orientation of bond vectors within the $C_nH_{2n+1}OH$ molecule, $R_r = an^{1/2}$.

Therefore,

$$\omega = [24akT/mR_r^3]^{1/2} = K'_r T^{1/2} n^{-3/4} \quad (7)$$

or, corresponding to Eq. (5),

$$\log n = -(4/3) \log f_m + (4/3) [\log K_r + \tfrac{1}{2} \log T]. \quad (8)$$

Therefore for a random coil conformation of the alcohol molecule the model yields a linear equation with a slope of -4/3.

COMPARISON OF THEORY AND EXPERIMENT

Experimental measurements were made for a homologous series of normal (aliphatic) alcohols using TDDS [3]. Cole's [4,5] multiple reflection technique in which the liquid alcohol is placed between the conductors at the open termation of a coaxial transmission line was used for these measurements. Details of the techniques and apparatus have been described elsewhere [3,6]. The relevant experimental data are shown in Fig. 2. Although the instrumental frequency range was from about 1 to 4000 MHz, a Cole-Cole type analysis allowed the estimation of static permittivities with surprisingly good results, as indicated by comparison with literature values in Table 1. Also given in Table 1 are the magnitudes and frequencies of the maximum loss peaks (ε''). These peaks of ε'' are the points of interest in the comparison of the tumbling model for relaxation and the experimental results.

The frequencies f_m of the maximum loss peaks are given in Fig. 3 as a log n vs log f plot. Also shown in Fig. 3 are straight lines of slope -2/3 and -4/3 as predicted by the tumbling model, corresponding to a fully extended molecule and a random coil molecule, respectively. The dots agree with the line of -2/3 slope quite well indicating that the alcohol molecules studied assume a fully extended conformation.

CONCLUSIONS

The relaxation of a homologous series of alcohols has been modeled using a simple tumbling model in which the molecular chain can assume either a fully extended or random coil conformation. A comparison with experimental data indicates that all of the alcohols studied (up to $C_{12}H_{25}OH$, dodecanol) behave as fully extended molecules at the temperature at which librational motion goes over into rotation. Such results were not unexpected for the shorter alcohols, however, for the longer molecules it had been anticipated that the data would scatter between the straight lines in Fig. 3, as the random coil conformation seemed to be more likely for longer chains.

The results for the complex permittivity of this quasi-polymeric series of alcohols and the discussion of these results shows that Cole's method is a powerful tool for studying the dielectric behavior of polar liquids. Although one would not expect such a simplified model to yield quantitative results, it appears that this one almost does and suggests that the activated (tumbling) polar molecules tend to have an extended orientation of bonds rather than a random coil configuration.

An interesting extension of this work would be to look experimentally at successively longer molecules and compare the results with the relaxation model developed in this paper. Likewise, the use of molecules, such as the named alcohols as diffusants in polymeric liquids and solids should be an

interesting topic for investigation by TDDS methods.

ACKNOWLEDGMENTS

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FIGURE CAPTIONS

Fig. 1. Schematic illustrating the fully extended chain model for an alcohol molecule. CH_2-mass = m $\simeq$ OH-mass. Linear density $\simeq$ m/a.

Fig. 2. ε' and ε'' as measured using TDDS for a homologous series of alcohols.

Fig. 3. Comparison of the model with experimental data. The dashed line of slope -4/3 corresponds to a random coil conformation whereas the solid line of slope -2/3 corresponds to the fully extended molecule. The data, shown as squares, indicate agreement with the fully extended molecular model.

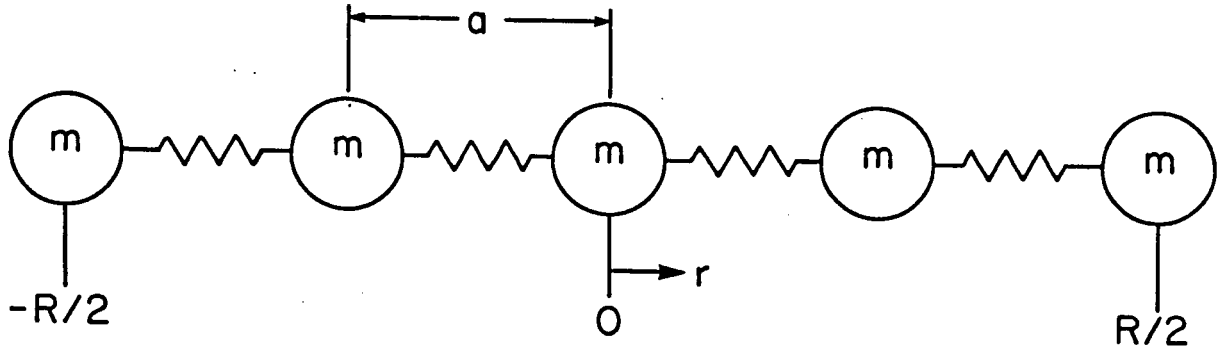
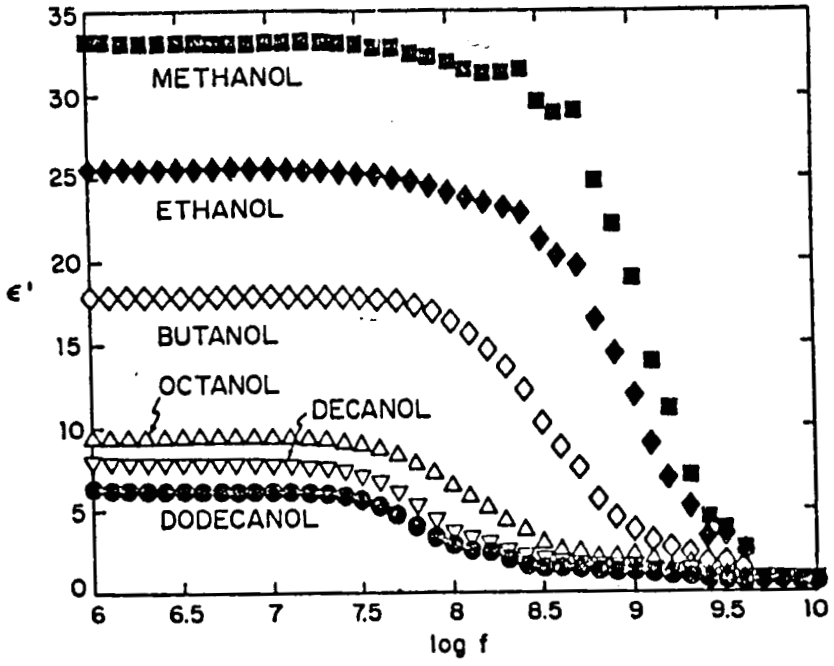


FIG. 1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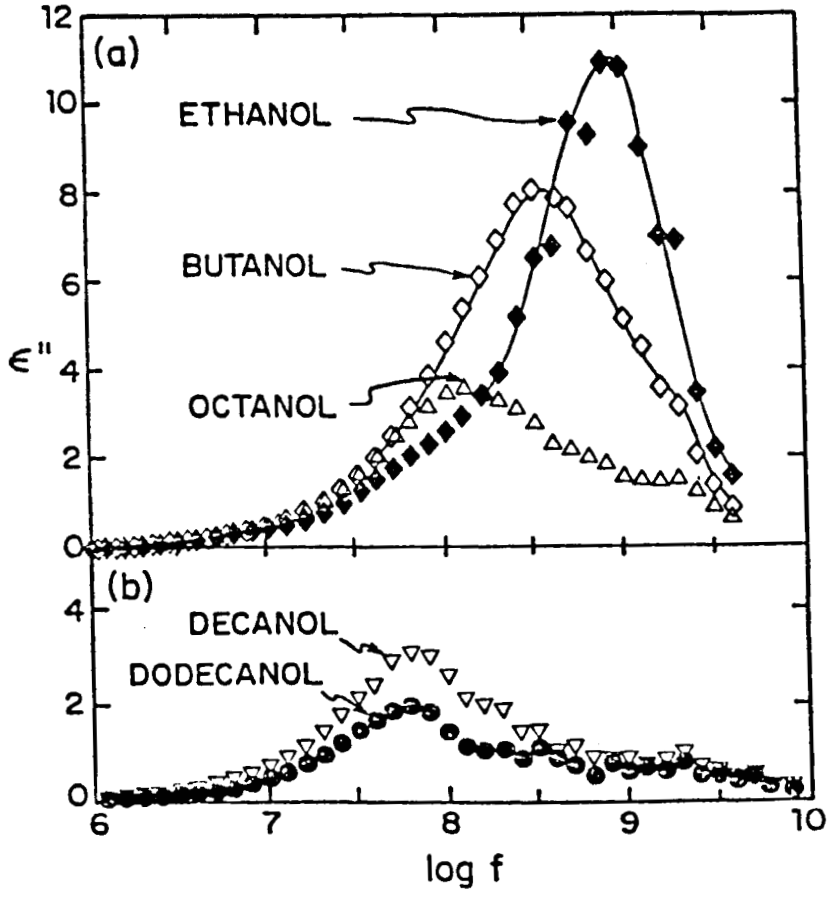
12
10
8
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(a)
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ETHANOL
BUTANOL
OCTANOL
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DECANOL
DODECANOL
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Fig 2

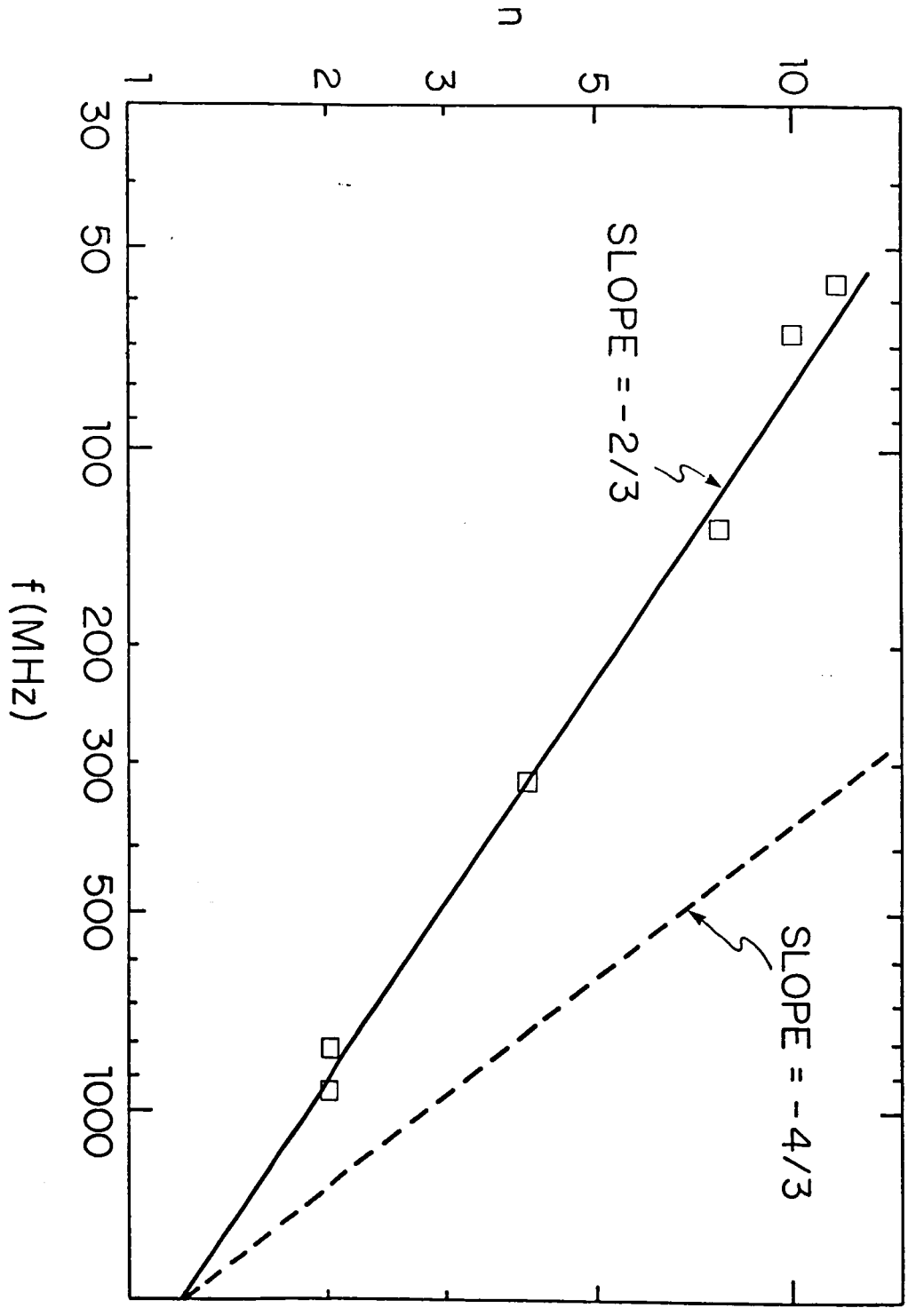

Fig. 2